DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]About the electroluminescence (electroluminescence) element which has a luminous layer which consists of organic compounds, this inventions differ in a conventional incandescent lamp, a fluorescent lamp, or a light emitting diode etc., and relate to organic electroluminescence devices which enable realization of the surface state photogen of a large area, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]Generally electroluminescence devices equip inter-electrode [two] with an electron hole transporting bed and a luminous layer, the electron hole supplied from an anode electrode through an electron hole transporting bed and the electron supplied from the cathode electrode of another side recombine by the interface of the above-mentioned luminous layer and an electron hole transporting bed, a singlet exciton is generated, and the above-mentioned luminous layer emits light.
[0003]By the way, as such electroluminescence devices, the electroluminescence devices of an inorganic system which used inorganic system fluorescent substances, such as selenium sulfide and zinc sulfide, for the luminous layer were common conventionally. However, the organic electroluminescence devices made to emit light as a luminous layer using organic coloring matter came to be proposed in recent years (refer to JP,59-194393,A).
[0004]And in [for example] above-mentioned JP,59-194393,A as a method of manufacturing such organic electroluminescence devices, The luminous layer which becomes inter-electrode with vacuum deposition from an electron hole transporting bed (electron hole injection zone) and organic coloring matter is provided one by one, voltage is impressed to this, and the method of obtaining the electroluminescence devices which emit light by less than 25V with the electric power transformation efficiency which attains to 9×10^{-5} (W/W) at least is proposed.

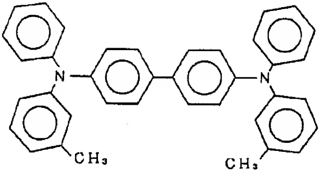
[0005]To JP,2-255789,A, the anode, an electron hole transporting bed (electron hole injection zone), a luminous layer, a hole blocking layer, the order of the negative pole, or this method of laminating one by one conversely and obtaining a light emitting device is indicated by the vacuum deposition method or the applying method. In that case, by using a naphthalene derivative for a luminous layer, an efficient luminous layer is obtained also by the low voltage, and the organic electroluminescence devices which have sufficient luminosity are obtained.
[0006]To JP,2-223188,A, by the wet producing-film methods, such as casting method and a spin coat method. The mixture layer of a hole transporting material (electron hole injection zone) and a luminescent material or the mixture layer of an electron transport material and a luminescent material is formed on the anode, and the method of vapor-depositing the negative pole subsequently and obtaining a light emitting device is indicated.
[0007]
[Problem(s) to be Solved by the Invention]By the way, in order to attain utilization of the above-mentioned organic electroluminescence devices as a source of sheet-like light of a large area unlike punctiform [, such as an incandescent lamp, a fluorescent lamp, or a light emitting diode,] or a linear light source, these organic electroluminescence devices are stabilized over a long period of time, and it is necessary to maintain high-intensity luminescence.
[0008]However, in the organic electroluminescence devices indicated to JP,59-194393,A, JP,2-255789,A, and JP,2-223188,A which were mentioned above, Although all showed value sufficient as an initial value of light emitting luminance, sufficient performance **** thing was not obtained in respect of the stability of light emitting luminance, or a luminescence life.
[0009]That is, in the above-mentioned conventional technology, each has only laminated simply the electrode (anode)-organic compound layer (two-layer or three layers containing monolayer or charge transfer layer)-electrode (negative pole) by this turn or this reverse order. Among these, since membrane structure changes easily in the case of the film produced with the vacuum deposition method and it becomes impossible to maintain the convenient electronic state for luminescence temporally simply to it with the heat which an organic compound receives in the case of an element drive, decline in luminous efficiency and the fall of a luminescence life are brought about.
[0010]Since structure changes like the film which produced the membrane structure which comprises a process in which a solvent molecule is removed by evaporation with the vacuum deposition method even when using the wet producing-film methods, such as casting method and a spin coat method, among conventional technologies, What shows stability and performance sufficient in respect of a life was not obtained.
[0011]In view of the actual condition of the above-mentioned conventional technology, in the low voltage, the purpose of this invention is efficient, and there is in providing organic

electroluminescence devices which stabilize and emit light at a long period of time, and a manufacturing method for the same.
[0012]
[Means for Solving the Problem]This invention persons by using for a luminous layer an organic compound film with micro crystallite condensation structure produced by heat-treatment to achieve the above objects, as a result of inquiring wholeheartedly, In a low voltage, it is efficient, and finds out that an element which stabilizes and emits light at a long period of time is obtained, and came to complete this invention.
[0013]Namely, in organic electroluminescence devices which emit light when a luminous layer which consists of organic compounds is formed in inter-electrode [of a couple at least with transparent one side] and an invention concerning claim 1 impresses voltage, They are organic electroluminescence devices having the micro crystallite condensation structure which this luminous layer was heat-treated and produced.
[0014]It is a manufacturing method of organic electroluminescence devices, wherein an invention concerning claim 2 forms an organic compound film with vacuum deposition, it is more than 50 degreeC, and heat-treats this organic compound film at temperature below the melting point of that organic compound, makes micro crystallite condensation structure form and considers it as a luminous layer.
[0015]In this invention, an electrode and a luminous layer of a couple are a part which polymerizes mutually, and an electron hole and an electron recombine and emit light by a polymerization part by impressing voltage to the above-mentioned inter-electrode one. In addition to a luminous layer, it may have an electron hole transporting bed and an electron transport layer.
[0016]An example of a type section figure of electroluminescence devices concerning this invention is shown in drawing 1. drawing 1 -- order from the bottom -- the anode side transparent substrate (glass substrate) 1, the transparent electrode 2 for the anodes, the electron hole transporting bed 3, the luminous layer 4, and the negative pole -- public funds -- the group electrode 5 is shown.
[0017]Drawing 2 shows a vacuum evaporator typically. In this invention, although that by the side of the anode and the negative pole, ** et al. may be sufficient, about a side which takes out light, a substrate material, an electrode material, and a charge transfer material need transparency which a luminous wavelength may penetrate.
[0018]On an insulating substrate, organic electroluminescence devices are vacuum deposition methods, such as a vacuum deposition method, sputtering process, or a CVD method, and can be manufactured one by one by forming an anode electrode, the electron hole moving bed, an organic luminous layer, an electron transport layer, and a cathode electrode. It is also possible to form membranes and manufacture on an insulating substrate in reverse order (a

cathode electrode, an electron transport layer, an organic luminous layer, the electron hole moving bed, order of an anode electrode).
[0019]And as the above-mentioned insulating substrate, synthetic resin bases, such as glass substrates, such as soda lime glass and borosilicate glass, a silicon wafer or polycarbonate, an acrylic, and epoxy, etc. are applicable, for example.
[0020]As a transparent thin film electrode, it is usable among electrodes of the above-mentioned couple in each conventionally publicly known electrode, such as a translucent electrode which comprises transparent electrodes, such as SnO_2, InO_2, or ITO, gold, or nickel. On the other hand, other thin film electrodes can use a thin film of small metal of work functions, such as Mg, aluminum, Ag, In, Li, and Na, transparently. As for these metal thin film electrodes, it is preferred to have a thickness of 300 A or more.
[0021]An organic compound which shows fluorescence strong against a visible region as the above-mentioned luminous layer, and can form membranes with the above-mentioned vacuum deposition method is applicable, For example, pyrene, perylene, perylene derivatives, peri non derivatives, anthracene, metal phthalocyanines, non-metal phthalocyanines, porphyrins, a quinolinol metal complex, etc. can be used.
[0022]In this invention, it is more than 50 degreeC, and an organic compound film which formed membranes with the above-mentioned vacuum deposition method is heat-treated at temperature below the melting point of the organic compound, and micro crystallite condensation structure is formed. Preferably, it is good for more than 80 degreeC to heat-treat at temperature below 150 degreeC. If treatment temperature is too low, since the structural change of a thin film is very slow, it will be hard to be used as a process. If treatment temperature is too high, a structural change of a thin film will take place very quickly, and it will not become desired membrane structure, but will seldom change to what has unsettled efficiency of luminescence. As processing time, about 1 to 30 minutes is preferred.
[0023]About heat-treatment of a luminous layer, after luminous layer formation, before forming the following layer, it is possible also in also after forming total layers. The details were indicated in the example. As for the above-mentioned luminous layer, when these organic electroluminescence devices are provided with an electron transport layer, it is preferred to have a thickness of 30-1000 A, and when organic electroluminescence devices are not provided with an electron transport layer, it is preferred to have a thickness of 100-3000 A. It is desirable to form membranes at the rate of 1-20 A [/sec] .
[0024]Next, the above-mentioned electron hole transporting bed is constituted by electron hole transfer compound which can transmit an electron hole from the anode to the negative pole side efficiently appropriately in inter-electrode [to which an electric field was given], and its about 50-3000 A is desirable as the thickness.
[0025]Among such electron hole transfer compounds, as an inorganic compound, For

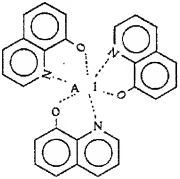
example, amorphous silicon membrane of P type which doped B (boron) can be used, and what is explained to the 13-14th columns of the 5-6th page and U.S. Pat. No. 4175960 of JP,59-194393,A can be used as another side and an organic compound, for example.
[0026]And as a desirable example of these electron hole transfer compounds, N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl 4,4'-diamine, 1,1'-bis(4-di-P-tolylamino phenyl) cyclohexane, 1,1'-bis(4-di-P-tolylamino phenyl)-4-phenyl-cyclohexane, Aromatic amine system compounds, such as 4,4''-bis(diphenylamino)KUWADORI phenyl, a bis(4-dimethylamino 2-methylphenyl)phenylmethane, N,N,N, and - Tori (P-tolyl) amine, are mentioned.
[0027]The above-mentioned electron transport layer blocks an electron hole from the anode in inter-electrode [to which an electric field was given], It is constituted by electron transport compound which can transmit an electron from the negative pole to the negative pole side efficiently appropriately, and about 50-3000 A is desirable like the above-mentioned electron hole transporting bed as the thickness.
[0028]Among such electron transport compounds, as an inorganic compound, N type amorphous silicon membrane which doped P (phosphorus), or CdS (n type), Can use compound semiconductor thin films, such as CdSe (n type), ZnS (n type), and ZnSe (n type), etc., and as another side and an organic compound, Triphenylmethane which has an amino group or its derivative, a xanthene, Various colors and paints, such as an acridine, an azine, thiazine, a thiazole, oxazine, and azo, Peri non system paints, perylene system paints, cyanine dye, 2,4,7-trinitro fluorenone, tetracyano quinodimethane, tetracyanoethylene, an oxadiazole derivative, etc. are mentioned.
[0029]
[Function]According to the invention concerning claim 1, since the micro crystallite condensation thin film of the organic compound which heat-treated to the luminous layer is used, to generation of heat by energization, etc., membrane structure is dramatically stable and shows the performance stable over the long time.
[0030]According to the invention concerning claim 2, since it is more than 50 degreeC and is heat-treating at the temperature below the melting point of the organic compound as conditions which heat-treat the organic compound film which carried out vacuum deposition, the luminous layer of optimum performance can be obtained.
[0031]
[Example]Hereafter, the example of this invention is described in detail.
[Example 1] As shown in drawing 1, the electron hole transporting bed 3 and the luminous layer 4 were formed in the 2nd page of the transparent electrode for the anodes of the borosilicate glass substrate 1 made from Matsuzaki Vacuum in which the transparent electrode 2 for the anodes which comprises an ITO film was formed. Heat-treatment of the luminous layer 4 was promptly performed to the evaporation apparatus shown in drawing 2 after

luminous layer formation using the attached substrate heating device 19. Heating conditions were made into 5 minutes by 120 degreeC.
[0032]the above-mentioned luminous layer 4 top -- further -- the negative pole -- public funds -- the group electrode 5 was laminated in this order, and it asked for the organic electroluminescence devices of the size of element-areas ^{2} of 0.25 cm (5 mm x 5 mm). The compound by which the material which constitutes the electron hole transporting bed 3 is expressed with N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl 4,4'-diamine (1), i.e., the following structural formula, The compound (melting point about 400degreeC) expressed with the following structural formula (2) among quinolinol metal complexes was used for the material which constitutes the luminous layer 4.
[0033]
[Formula 1]



(1)

[0034]
[Formula 2]



(2)

[0035]What vapor-deposited aluminum to antioxidizing was used for the metal electrode 5 for the negative poles on the vapor codeposition thin film of Mg:Ag=7:3. the average value of the resistance in the 2nd page of an ITO film -- the thickness of 10ohm/sq., the electron hole transporting bed 3, and the luminous layer 4 -- each -- 700 A and the negative pole -- public funds -- the thickness of the group electrode 5 is 1500 A -- element areas -- the negative pole -

- public funds -- the area of the group electrode 5 prescribed.
[0036]These organic electroluminescence devices are manufactured by the following methods. That is, ITO film 2 of the borosilicate glass substrate 1 surface made from Matsuzaki Vacuum was first etched into the desired pattern with 15wt% of the hydrochloric acid aqueous solution, pure water washed, subsequently steam cleaning of ethanol was performed, and it dried on condition of 100 **x10Hr with clean oven.
[0037]Next, the electron hole transporting bed 3 used the vacuum evaporator shown in drawing 2, and formed it with the boat heating method. Namely, about 60% of the central part of the compound beforehand expressed with said structural formula (1) is used, Laying this on the heating board 11 with a thermo couple, heating it, evaporating it, measuring the thickness and the vapor rate of the electron hole transporting bed 3 with thickness and the crystal oscillator 16 for vapor rate detection, and controlling the numerical aperture of the shutter 14. On ITO film 2 of the film formation board 10 which comprises the above-mentioned glass substrate 1 fixed to the electrode holder 10a, the electron hole transporting bed 3 which comprises a compound expressed with the above-mentioned structural formula (1) was formed. As for vacuum deposition conditions, below 5.0×10^{-7}torr. carried out the ultimate vacuum before vacuum evaporation.
[0038]Next, the luminous layer 4 was formed with the boat heating method within the same vacuum evaporator, without taking a break the vacuum of the vacuum evaporator of this drawing 2. That is, after carrying out recrystallization refining from a solvent, the compound expressed with vacuum clean oven with said structural formula (2) which removed the solvent was laid on the heating board 11 with a thermo couple, and the luminous layer 4 was formed on the electron hole transporting bed 3 of the film formation board 10 like the case of the above-mentioned electron hole transporting bed 3.
[0039]The vacuum deposition conditions are as follows.
the back pressure: -- below 5.0×10^{-7}torr. cooking temperature: -- 180-200 ** evaporation rate: -- 1-20 A/sec
The luminous layer 4 heat-treated promptly after luminous layer 4 formation further using the attached substrate heating device 19 to the evaporation apparatus shown in drawing 2. Heating conditions were made into 5 minutes by 120 degreeC.
[0040]the inside of the same vacuum evaporator -- an electron beam heating process -- the negative pole -- public funds -- the group electrode 5 was formed. Namely, a metallic raw material is laid in the crucible 12 for the product electron beam heating vacuum evaporation made from BN, heating with the electron gun 13 and making it evaporate -- thickness and the crystal oscillator 17 for vapor rate detection -- the negative pole -- public funds -- while measuring the thickness and the vapor rate of the group electrode 5 and controlling the numerical aperture of the shutter 15 -- the luminous layer 4 top of the film formation board 10 --

the negative pole -- public funds -- the group electrode 5 was formed. 18 show the mask among the figure.
[0041]The vacuum deposition conditions of the metal electrode 6 for the negative poles are as follows.

the back pressure: -- below $5.0x10^{-7}$torr. filament current: -- 30-35-mA evaporation rate: -- 1-10 A/sec
[Example 2] In Example 1, after luminous layer 4 formation, all the films were heat-treated in the atmosphere after the end of formation without heat-treating promptly. That is, after producing electroluminescence devices, in the room temperature atmosphere, the heater heating device was used and the luminous layer 4 was heat-treated. Heating conditions were made into 120 degreeCx 5 minutes.
[Comparative example 1] In Example 1, all the films were formed and it was considered as electroluminescence devices without heat-treating after luminous layer 4 formation.
[Example 3] Conversely [Example 1], the film was formed in order of the negative pole side board, the electrode for the negative poles, the luminous layer, the electron hole transporting bed, and the transparent electrode for the anodes, and electroluminescence devices were produced.
[0042]The commercial silicon wafer was used for the negative pole side board. Before use, after forming an insulator layer by SiO_2, pure water washed, subsequently steam cleaning of ethanol was performed, and the thing dry with clean oven was used.
[0043]Using the same material as Example 1, similarly, the vacuum deposition method was used for the metal electrode for the negative poles with electron beam heating, and it formed it on the negative pole side board. Thickness could be 300 A or more. As for vacuum deposition conditions, below $5.0x10^{-7}$torr. carried out the ultimate vacuum before vacuum evaporation.
[0044]The luminous layer was similarly formed using the same material as Example 1. It heat-treated on the conditions for 120 degreeCx 5 minutes like Example 1 after luminous layer formation. The electron hole transporting bed formed the same material as Example 1 on the luminous layer similarly.
[0045]The transparent electrode for the anodes was used as the golden (Au) translucent electrode. Like Example 1, the vacuum deposition method by electron beam heating was adopted, and it formed on the electron hole transporting bed. Thickness could be 300 A or more.
[Example 4] In Example 3, after luminous layer formation, all the films were heat-treated in the atmosphere after the end of formation without heat-treating promptly. That is, after producing electroluminescence devices, in the room temperature atmosphere, the heater heating device was used and the luminous layer was heat-treated. Heating conditions were made into 120

degreeCx 5 minutes.

[Comparative example 2] In Example 3, all the films were formed and it was considered as electroluminescence devices without heat-treating after luminous layer formation.

[0046]The result of having measured the initial luminance characteristic and luminosity half-life is shown in Table 1 about each element of the above-mentioned example and a comparative example.

[0047]

[Table 1]

	初期特性（１０Ｖでの輝度）	輝度半減期
実施例１	７１０　ｃｄ／㎡	２０　Ｈｒ
実施例２	６８０　ｃｄ／㎡	１８　Ｈｒ
比較例１	７００　ｃｄ／㎡	０．２５　Ｈｒ
実施例３	８７０　ｃｄ／㎡	２５　Ｈｒ
実施例４	８５０　ｃｄ／㎡	２４　Ｈｒ
比較例２	８５０　ｃｄ／㎡	０．４　Ｈｒ

[0048]Table 1 shows that the organic electroluminescence devices of this invention are markedly alike, and luminosity half-life is excellent.

[0049]

[Effect of the Invention]Since a luminous layer is heat-treated and has micro crystallite condensation structure, to generation of heat by energization, etc., the organic electroluminescence devices of this invention are dramatically stable, and can show the luminescent ability stable over the long time.

[0050]Since the luminous layer is heat-treated on the optimal heat-treatment conditions, manufacturing efficiency is good and can use it as the organic electroluminescence devices of the outstanding performance.

[Translation done.]